DETERMINATION OF PARTICULATE MATTER AND NICOTINE DELIVERIES OF CIGARETTES*

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A collaborative smoking study for the determination of particulate matter (PM) and nicotine deliveries of cigarette smoke was completed during the year. The Analytical Methods Committee of the Tobacco Chemists Conference chose the method to be tested. The proposed method is a compromise of the various procedures now in use by the tobacco companies and related industries engaged in the analysis of cigarette smoke. The committee members believe the method is as reliable a method for the determination of particulate matter and nicotine deliveries of cigarettes as can be prepared at the present time.

One carton each of two different cigarettes, King non-filter cigarette and King filter cigarette, made for this study

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were sent to each collaborator with a copy of the proposed method. Each collaborator was asked to smoke forty cigarettes instead of 20 for this study. In addition to particulate matter (PM), and nicotine deliveries, cigarette total puff count was determined for each brand. No correction was made for moisture contained in the particulate matter.

PROCEDURE

SAMPLE SELECTION

Remove cigarettes from 5 randomly selected packages, place them in tray or wire basket and condition them for 24 hrs. at 75 ± 2°F. and 60 ± 2% relative humidity (60% relative humidity can be obtained by placing solution containing 26% water and 74% absolute glycerine by weight - ref. index = 1.437 and 20°C. - in closed desiccator). Determine average weight of 50 randomly selected, conditioned cigarettes. Select 20 cigarettes weighing within ± 20 mg. of average weight. Cigarettes must not contain soft spots nor be loosely packed or frayed at either end. Mark each cigarette 30 mm. from butt end with soft lead pencil or pen without puncturing paper. Store selected cigarettes at 75°F. and 60% r.h. until they are to be smoked. If sample selection is made in room not maintained at 75 ± 2°C. and 60 ± 2% r.h. cigarettes must be reconditioned for 4 hrs. before smoking. (It is recommended that cigarette sample selection and the cigarette smoking

be carried out in a laboratory room maintained at 75 ± 2°F. and 60 ± 2% r.h.).

SMOKING MACHINE CHARACTERISTICS

Smoking machines must be automatic and capable of drawing puffs according to following specifications:

Puff volume - 35 ± 0.5 ml. measured as volume of smoke that will be drawn from cigarette under actual machine smoking conditions. Puff volume should be checked before and after each smoking run with smoke collection trap in system. Puff volume may be measured by water filled 50 ml. burette and leveling bulb. Water levels in burette and bulb should be equal at start and finish and as nearly equal during puff as possible.

Puff duration - 2 ± 0.2 sec. measured at cigarette under actual machine smoking conditions by hot wire anemometer or soap bubble manometer.

Puff frequency - 1 puff per 60 ± 1 sec.

Cigarettes must be free from drafts (other than normal convection) while being smoked.

PARTICULATE MATTER

Apparatus

Filter holder - A lucite (or aluminum) filter holder consisting of threaded inner and outer part and Teflon gasket.

Filter disc - Cut discs 1.74" (44mm.) in diameter from CM

113 fiber glass sheet made by the Cambridge Filter Corporation, 738 Erie Boulevard, East Syracuse 3, New York. Filters must collect at least 99% of all particles 0.3 microns in diameter and over.

Lucite guide - A lucite guide, is used to assist in placing rubber membrane on filter holder. (The holder, guide, and filter medium, CM 113, both in sheet form and as 1.74" diameter discs, are obtainable from Phipps and Bird, Inc., Richmond, Virginia.)

Rubber membrane - Cut square piece of medium latex dental dam, approximately 3.5 x 3.5 cm. Place between two pieces of rubber tile, or other suitable material, and punch hole 4 to 6 mm. in diameter in center of sheet with cork borer of appropriate size; size of hole will depend on circumference of cigarettes. Latex rubber sleeves, 8 mm. in diameter and 20 mm. long may also be used.

Rubber "O" ring - "O" ring with I.D. of 3/8" may be made by slicing off thin section of 3/8" I.D. rubber tubing or may be purchases from Linear, Inc., State Road and Levick Street, Philadelphia, Pennsylvania.

Cambridge filter assembly - For a detailed description of smoking apparatus see Wartman, W. B., Cogbill, E. C., and Harlow, E. S., Anal. Chem., Vol. 31, pp. 1705-9, (1959).

Determination

Using Lucite guide, place rubber membrane on filter holder

by inserting offset end of Lucite guide through hole in rubber membrane and thence into entrance tube of filter holder, holding guide and membrane firmly against filter holder, roll rubber "O" ring over guide and into position around membrane and in groove on entrance tube. In some instances it may be necessary to center aperture and adjust its diameter by manipulating rubber membrane. Excess rubber membrane is trimmed with scissors. Fit glass fiber filter disc into filter holder with rough side toward port through which cigarette is inserted. After positioning Teflon gasket with flat side resting against filter disc, screw Lucite plug in securely against gasket. Tighten with special wire wrench with ends fitted into two sockets on back of plug.

Wipe gently with soft cloth or tissue and weigh filter assembly to nearest 0.2 mg. Connect filter assembly to smoking machine with short piece of rubber or other suitable tubing having sufficiently heavy wall that cigarette and filter assembly will be held in horizontal position. Keep volume between filter holder and machine to minimum. (Do not use surge flask in smoking machine assembly.) Test smoking apparatus and filter assembly for leaks. Insert cigarette through hole in rubber membrane until end of butt is approximately flush with inner end of holder tube, i.e. to depth of approximately 7/16". Care must be taken that butt end does not come in contact with filter disc. Cigarette is withdrawn slightly so that lip of

orifice in rubber membrane projects outward and forms a snug-fitting collar without crimping or pinching cigarette. Occasionally, it may be necessary to shift position of cigarette slightly in or out, to insure that collar surrounds smooth portion of cigarette and provides leak-free seal.

Light cigarette at beginning of first puff (an electric coil lighter is suggested). Smoke each cigarette until burning coal reaches 30 mm. mark. If operator anticipates that coal will reach 30 mm. mark during puff, he should use judgment whether to allow cigarettes to burn beyond mark or to stop smoking it short of mark. In the smoking of cigarettes "overs" should be balanced with "unders" for each filter. After last puff, allow cigarette to remain in holder, free burning, until few seconds before next puff will be drawn by machine, then quickly remove butt from holder and allow clearing puff of air to draw in smoke remaining in entrance port of assembly. In same manner, smoke total of five cigarettes through filter. Immediately after five cigarettes have been smoked, disconnect filter assembly from apparatus, wipe and weigh to the nearest 0.2 mg.

Record gain in weight of filter assembly. (Save smoke samples for "nicotine" analysis.) Calculate particulate matter (wet) by:

$$\text{wt. PM (wet)/cigarette} = \frac{\text{gain in wt. of filter assembly (mg.)}}{5}$$

Smoke 4 samples of 5 cigarettes each and average results.

ALKALOIDS (AS NICOTINE) USING MODIFIED KJELDAHL STILL

Reagents

Hydrochloric acid - 0.1 N.

Hydrochloric acid - 1 part conc. HCl to 11 parts water.

Sodium hydroxide-sodium chloride soln. - NaOH solution 30% by weight saturated with NaCl.

Apparatus

Steam distillation apparatus - Kjeldahl flask, 500 ml. fitted with steam tube, trap and condenser.

Volumetric flask - 500 ml.

Spectrophotometer - Beckman DU or other instrument capable of accurately measuring absorbance in 200-300 mμ range and having slit width not greater than 5 mμ.

Determination

Transfer filter disc containing particulate matter to Kjeldahl flask and add 50 ml. of 0.1 N HCl. Wipe out entrance chamber of filter holder with two small swabs of cotton or pieces of CM 113 filter held in forceps, and add them to flask. Fit flask for steam distillation with steam inlet tube, spray trap and condenser. Steam distill acid solution for 10-15 min. keeping volume approximately constant by applying additional heat. Discard condensate. Stop steam distillation, place 500 ml. volumetric flask containing 25 ml. of 1 + 11 HCl

under condenser with condenser tip dipping into acid solution and add 25 ml. of NaOH-NaCl solution to distillation flask and connect immediately. Keeping volume in distilling flask between 75 and 100 ml., rapidly steam distill until volume of distillate is ca 450 ml., then add water to mark and mix. Determine absorbance of distillate at 236, 259 and 282 mμ against blank of 0.1 H HCl using 1 cm. cells.

Calculate total weight of "nicotine" in smoke sample as follows:

$$A'_{259} = 1.059 \left[A_{259} - 1/2 \, (A_{236} + A_{282}) \right]$$

A'_{259} = absorbance of "nicotine" corrected for background

$$\text{Total wt. "nicotine" (mg.)} = \frac{A'_{259} \times 500}{a \times b}$$

where a is absorptivity of nicotine in 0.1 N HCl solution and b is cell length.

Determine a by $a = \frac{A}{c \times b}$ where A is absorbance at 259 mμ and c is concentration in g./l. of standard solution of pure nicotine in 0.1 N HCl. Nicotine should be purified by repeated distillation until physical constants reach constant values which agree with those for pure nicotine.

$$\text{Wt. "nicotine" (mg.)/cigarette} = \frac{\text{total wt. "nicotine" (mg.)}}{5}$$

Make separate analysis on each filter.

ALKALOIDS (AS NICOTINE) USING GRIFFITH STILL

Reagents

Hydrochloric acid - 0.2 N.

Hydrochloric acid - 1 part conc. HCl to 9 parts water.

Sodium hydroxide - sodium chloride soln. - NaOH solution 30% by weight saturated with NaCl.

Apparatus

Steam distillation apparatus - Griffith still may be obtained from Consolidated Glass Works, Inc., Kingsport, Tenn.

Volumetric flask - 250 ml.

Spectrophotometer - Same as under modified Kjeldahl still.

Determination

Transfer filter disc containing particulate matter to Griffith still and add 5 ml. of 0.2 N HCl. Wipe out entrance port of each filter with two small cotton swabs or pieces of CM 113 filter held in forceps and add them to flask. Rapidly steam distill acid solution, collecting about 100 ml. of distillate, keeping volume approximately constant. Discard condensate. Turn off steam, place 250 ml. volumetric flask containing 10 ml. of 1 + 9 HCl under condensate with condenser tip dipping into acid solution, add 5 ml. of NaOH-NaCl solution. Keeping volume in flask approximately constant, rapidly distill ca 225 ml., add water to mark and mix. Proceed as under directions for modified Kjeldahl still beginning with "Determine absorbance of distillate .....", (Factor for calculatic of total wt. "nicotine" (mg.) use X 250 in place of X 500).

RESULTS

The collaborators were asked to determine the average weight of each cigarette brand after being conditioned for 24 hours at 75 ± 2°F and 60 ± 2% relative humidity and the average weight of tobacco burned. (Obtained by cutting off the 30 mm cigarette butt and weighing the remaining cigarette rods including the cigarette paper weight.) Table 1 shows average cigarette weight, average weight of tobacco burned, the mean weights of two cigarettes, the interlaboratory standard deviations, and the coefficient of variation in percent as obtained by the twelve collaborators. As would be expected cutting off the 30 mm cigarette butt resulted in a higher coefficient of variation in the weight of tobacco burned than that obtained for the cigarette weight; i.e., 0.9 to 1.1 and 1.6 to 1.9, respectively.

The collaborators were instructed to smoke eight ports (samples) of each brand, a total of 40 cigarettes per brand. The average total number of puffs per five cigarettes, and standard deviation for the first four of the eight ports and the eight ports (samples of 5 cigarettes) as obtained by the twelve collaborators are shown in Table 2. The mean coefficients of variation, within and between the laboratories are also shown in this table. The non-filter cigarette had a higher variation in the total puff count than the filter cigarette. The between laboratories variation was twice that obtained within laboratories.

The particulate matter and nicotine deliveries (wet), for the two cigarette brands, are shown in Tables 3 and 4. The standard deviations obtained by each collaborator for the first four of the eight ports and the eight ports are included in these tables together with the mean coefficients of variation within and between laboratories. The coefficients of variation between laboratories for particulate matter was about 3 times and for nicotine about 2 times that within laboratories. Furthermore, the collaborators did not obtain a higher degree of precision by increasing the number of samples (ports of 5 cigarettes) from four to eight. Thus, the prescribed procedure of four samples per cigarette brand is satisfactory.

DISCUSSION

The coefficients of variation obtained within the twelve collaborators on total puff count (eight samples), particulate matter (four and eight samples), and nicotine deliveries were less than five percent. This is a reasonable value when the nature of the sample and number and type of variables are considered. However, the coefficients of variation obtained between the twelve collaborators for particulate matter and nicotine were approximately ten percent. Inspection of the data shows that the particulate matter and nicotine deliveries of two of the collaborators were significantly lower than the averages of the collaborators and two collaborators' results were significantly higher than the averages. Three of these

four laboratories had puff counts significantly higher than the remaining laboratories which would indicate differences in their smoking machines. The remaining laboratory with different results had cigarettes which weighed significantly lower than the cigarette averages obtained by the twelve collaborators. This collaborator also had puff counts which were significantly lower than the average puff counts. Therefore, we believe that we are justified in recalculating the data without collaborators No 1, No 8, No 22, and No 23. Collaborator No 1's smoking machine definitely is different from the other collaborators, he obtained the highest puff count and among the lowest particulate matter and nicotine deliveries. Collaborator No 8's cigarettes obviously were drier than the other collaborators' cigarettes, burned faster and delivered less particulate matter and nicotine than the average obtained by the collaborators. Collaborators No 22 and No 23's smoking machines appear to be different from the other collaborators'; they obtained high puff counts and significantly higher particulate matter and nicotine deliveries than the other collaborators.

The average values obtained by the eight collaborators are not different from the average values obtained by the twelve collaborators, Table 5. The coefficients of variation between the eight collaborators, however, are less than five percent for particulate matter delivery and approximately five percent for nicotine. The coefficients of variation are summarized in Table 6.

RECOMMENDATION

It is recommended that the proposed cigarette smoking method for the determination of particulate matter and nicotine deliveries of cigarettes be accepted as first action method by the Association of Official Agricultural Chemists.

TABLE 1

AVERAGE WEIGHT OF EQUILIBRATED (85 mm.) CIGARETTES AND WEIGHT OF TOBACCO BURNED (30 mm. butt), GRAMS

	Non-Filter		Filter	
Coll. No.	Cigarette Weight	Tobacco Burned	Cigarette Weight	Tobacco Burned
1	1.195	0.766	1.106	0.769
2	1.208	0.759	1.125	0.768
3	1.196	0.759	1.116	0.763
5	1.202	0.780	1.114	0.786
8	1.178	0.768	1.090	0.761
9	1.203	0.781	1.124	0.769
11	1.196	0.774	1.115	0.774
13	1.210	0.775	1.123	0.763
20	1.196	0.797	1.113	0.801
22	1.197	0.769	1.117	0.765
23	1.214	0.780	1.112	0.780
24	1.231	0.801	1.124	0.788
Mean	1.202	0.775	1.115	0.774
Std. Dev.	0.013	0.015	0.010	0.012
Coeff. of Var. %	1.1	1.9	0.9	1.6

TABLE 2

AVERAGE TOTAL NUMBER OF PUFFS PER FIVE CIGARETTES, (85 mm.)

Coll. No.	Non-Filter				Filter			
	No. of Puffs		Std. Dev.		No. of Puffs		Std. Dev.	
Ports	8	4	8	4	8	4	8	4
1	59	59	0.5	0.6	53	53	0.7	0.8
2	48	48	1.5	1.7	48	49	1.6	1.6
3	52	52	1.3	0.6	50	50	0.0	0.0
5	49	50	1.0	1.0	47	48	1.7	1.7
8	46	46	0.9	0.8	45	45	0.4	0.0
9	51	50	2.2	1.4	49	49	1.4	1.9
11	50	50	0.4	0.0	50	50	0.0	0.0
13	50	49	1.1	0.8	48	48	1.6	1.0
20	50	50	1.6	2.2	50	50	1.4	1.7
22	55	55	1.4	1.1	53	54	1.4	1.1
23	55	55	0.5	0.6	52	52	1.3	1.5
24	51	49	2.0	1.0	48	49	0.5	0.6
Mean	51.3	51.0	1.31*	1.13*	49.5	49.6	1.16*	1.22*
Coefficients of Variation								
Within			2.6%	2.2%			2.3%	2.5%
Between			6.9%	6.9%			5.0%	4.8%
Mean Standard Deviation Between Laboratories								
			3.52	3.54			2.47	2.38

* Mean Standard Deviation within Laboratories

TABLE 3

PARTICULATE MATTER DELIVERY PER CIGARETTE, MILLIGRAMS

Coll. No.	Non-Filter Particulate Matter		Non-Filter Std. Dev.		Filter Particulate Matter		Filter Std. Dev.	
Ports	8	4	8	4	8	4	8	4
1	26.0	26.2	0.64	0.91	22.8	22.5	0.59	0.69
2	30.4	30.8	1.35	1.78	23.8	23.8	1.01	0.25
3	31.7	31.8	0.75	0.62	24.8	25.1	0.55	0.22
5	30.4	30.6	0.87	0.99	22.3	22.9	1.14	1.12
8	28.9	29.6	1.71	1.08	21.2	20.9	0.72	0.61
9	33.0	32.8	1.13	0.13	24.3	23.8	0.94	1.03
11	33.6	33.4	0.61	0.73	25.7	25.5	0.64	0.49
13	31.8	31.7	0.39	0.22	23.3	23.2	0.42	0.48
20	31.9	32.2	0.67	0.73	24.0	24.3	0.83	0.77
22	37.4	37.9	1.78	2.27	28.6	28.5	0.34	0.40
23	37.1	37.3	1.11	1.57	29.6	29.7	1.31	1.47
24	33.9	33.2	0.95	0.14	25.1	25.3	0.43	0.54
Mean	32.2	32.3	1.08*	1.13*	24.6	24.6	0.80*	0.76*
Coefficient of Variation								
Within			3.4%	3.5%			3.2%	3.1%
Between			9.9%	9.8%			10.0%	10.0%
Mean Standard Deviation Between Laboratories								
			3.19	3.15			2.45	2.48

* Mean Standard Deviations within Laboratories

TABLE 4

NICOTINE DELIVERY PER CIGARETTE, MILLIGRAMS

Coll. No.	Non-Filter Nicotine		Non-Filter Std. Dev.		Filter Nicotine		Filter Std. Dev.	
Ports	8	4	8	4	8	4	8	4
1	1.24	1.24	0.07	0.06	1.11	1.12	0.05	0.07
2	1.47	1.44	0.08	0.10	1.22	1.22	0.04	0.01
3	1.63	1.60	0.05	0.04	1.29	1.30	0.03	0.02
5	1.51	1.49	0.05	0.07	1.22	1.21	0.08	0.12
8	1.57	1.59	0.09	0.06	1.19	1.17	0.03	0.02
9	1.62	1.63	0.09	0.13	1.28	1.27	0.05	0.07
11	1.65	1.62	0.05	0.04	1.34	1.32	0.06	0.08
13	1.55	1.55	0.02	0.03	1.18	1.18	0.02	0.03
20	1.47	1.43	0.06	0.04	1.17	1.17	0.03	0.03
22	1.73	1.75	0.04	0.03	1.41	1.41	0.03	0.03
23	1.80	1.81	0.06	0.08	1.47	1.51	0.09	0.05
24	1.59	1.59	0.04	0.05	1.23	1.20	0.07	0.08
Mean	1.57	1.56	0.061*	0.066*	1.26	1.26	0.054*	0.060*

Coefficient of Variation

Within	3.9%	4.2%	4.3%	4.8%
Between	9.1%	9.6%	8.2%	9.0%

Mean Standard Deviation Between Laboratories

0.143	0.149	0.103	0.114

* Mean Standard Devaition within Laboratories

TABLE 5

TOTAL PUFF COUNT, PARTICULATE MATTER AND NICOTINE DELIVERIES OF CIGARETTES FOR EIGHT COLLABORATORS*, FOUR PORTS

	Non-Filter			Filter		
	mg./ Cigt.	Std. Dev.	Coef. Var.,%	mg./ Cigt.	Std. Dev.	Coef. Var.,%
Total Puff Count						
Within Labs.	49.7	1.26	2.5	49.0	1.31	2.7
Between Labs.	49.7	0.95	1.9	49.0	0.80	1.6
Particulate Matter						
Within Labs.	32.0	0.84	2.6	24.2	0.69	2.8
Between Labs.	32.0	1.04	3.2	24.2	1.00	4.1
Nicotine						
Within Labs.	1.54	0.071	4.6	1.23	0.066	5.4
Between Labs.	1.54	0.081	5.2	1.23	0.055	4.5

* Omitting collaborators No 1, No 8, No 22, and No 23.

TABLE 6

SUMMARY OF COEFFICIENTS OF VARIATION, %,

WITHIN AND BETWEEN LABORATORIES

	Within Laboratories		Between Laboratories	
	Non-Filter	Filter	Non-Filter	Filter
Twelve Collaborating Laboratories				
Cigarette Weight	---	---	1.1	0.9
Tobacco Burned	---	---	1.9	1.6
Total Puff Count	2.6	2.3	6.9	5.0
Particulate Matter				
(8 ports)	3.4	3.2	9.9	10.0
(4 ports)	3.5	3.1	9.8	10.0
Nicotine				
(8 ports)	3.9	4.3	9.1	8.2
(4 ports)	4.2	4.8	9.6	9.0
Omitting Laboratories 1, 8, 22 and 23				
Total Puff Count				
(4 ports)	2.5	2.7	1.9	1.6
Particulate Matter				
(4 ports)	2.6	2.8	3.2	4.1
Nicotine				
(4 ports)	4.6	5.4	5.2	4.5